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(54) **AGENT DE REVETEMENT AQUEUX A DEUX COMPOSANTS ET SON UTILISATION**

(54) **AQUEOUS TWO-COMPONENT COATING AGENT AND USE THEREOF**

(57) L'invention concerne un agent de revêtement aqueux à deux composants à base d'un ou plusieurs polyols et d'un ou plusieurs polyisocyanates, en particulier pour le revêtement de substrats en matière plastique, dans lequel le ou les polyols se présentent dans un premier composant et le ou les polyisocyanates se présentent dans un deuxième composant, et les composants sont mis en présence l'un de l'autre avant application. L'agent de revêtement renferme, une fois que les composants sont réunis, les constituants ci-après: 10 à 40 % en poids d'un ou plusieurs polyols dont la moyenne arithmétique des masses molaires est comprise entre 300 et 2 000 000, un indice d'OH de 10 à 400 mg KHO/g et une teneur atteignant 400 milliéquivalents/100 g de résine solide en groupes ioniques et/ou en groupes transformables en groupes ioniques, 0,5 à 10 % en poids d'une ou plusieurs oléfines chlorées et/ou non chlorées, 1 à 35 % en poids de pigments électroducteurs et/ou de charges, 5 à 30 % en poids d'un ou plusieurs solvants organiques, 25 à 75 % en poids d'eau et 1 à 30 % en poids de polyisocyanates ayant en moyenne au moins deux groupes isocyanates libres par molécule, la somme des constituants précités s'élevant à 100 % en poids et la proportion de composants polyisocyanates et de composants polyols étant choisie de façon que le rapport entre le nombre de groupes NCO réactifs et le nombre de groupes OH soit compris entre 5:1 et 0,5:1.

(57) The invention concerns an aqueous two-component coating agent based on one or a plurality of polyols and one or a plurality of polyisocyanates, in particular for coating plastics substrates, the polyol(s) being present in a first component and the polyisocyanate(s) being present in a second component and the components being combined before application. When the components have been combined, the coating agent comprises the following constituents: between 10 and 40 wt % of one or a plurality of polyols with a number average of the molecular mass of between 300 and 2,000,000, an OH number of between 10 and 400 mg KOH/g and a content of up to 400 milliequivalents/100 g of solid resin of ionic groups and/or groups which can be converted into ionic groups; between 0.5 and 10 wt % of one or a plurality of chlorinated and/or unchlorinated polyolefins; between 1 and 35 wt % of electrically conductive pigments and/or fillers; between 5 and 30 wt % of one or a plurality of organic solvents; between 25 and 75 wt % water; and between 1 and 30 wt % polyisocyanates with an average of at least two free isocyanate groups per molecule, the total of these constituents being 100 wt % and the quantitative proportion between the polyisocyanate component and the polyol component being such that the ratio between the number of reactive NCO groups and the number of OH groups is between 5:1 and 0.5:1.

An aqueous two-component coating composition and the use thereof

This invention relates to aqueous coating compositions based on polyols, in particular for coating plastic substrates, and to the use thereof.

Ever increasing quantities of mouldings made from plastic substrates, in particular from polyolefins, for example polypropylene in pure form or in modified form (PP blend), are being used in the automotive industry due to the excellent overall properties thereof in comparison with other plastics. The elevated content of organic solvents is increasingly being reduced by the development of water-based coating systems.

Aqueous coating compositions based on epoxy resins or acrylate resins as two-component systems are thus known from DE-A 41 23 860 or EP-A 0 358 979. However, adequate adhesion to the substrate is not achievable when coating plastic substrates, in particular polyolefin substrates which have not been pretreated. Moreover, defects such as pinholing occur in relatively thick films.

DE-A-39 10 901 describes aqueous coating compositions for plastic components, the compositions containing aqueous emulsions of acrylate resins or polyurethane resins, chlorinated polyolefins optionally together with pigments or additives. Production of these coating compositions is highly complex due to a special melting process for the chlorinated polyolefins and because of an azeotropic distillation stage for the organic solvent.
According to EP-A-0 539 710, aqueous keying primer compositions based on chlorinated polyolefins, organic solvent, emulsifiers and pigments and optionally a film

forming binder may be used for lacquer coating plastics. Application of lacquers containing solvent onto such priming layers, may cause the primer to dissolve, so resulting in lacquer faults.

EP-A-0 587 061 (H 32 088) describes an aqueous coating composition based on polyols, which composition moreover contains chlorinated polyolefins, organic solvent and optionally further binders, together with polyisocyanates. The composition may be used on plastic substrates as a primer, for single-layer lacquer coatings or as a base lacquer without prior priming. Usable pigments are titanium dioxide, talcum and carbon black. The coating composition provides good adhesion, in particular to polyolefin plastic substrates, together with a smooth, faultless surface.

Subsequent layers may also be applied in the conventional manner, such as for example by spraying, roller application, dipping. The coating composition is, however, not suitable for electrostatic application of subsequent layers.

The surface conductivity required for subsequent electrostatic coating layers may be achieved by using electrically conductive primers.

These contain, for example, electrically conductive carbon black or graphite (*c.f. Glasurit-Handbuch* from BASF Lacke + Farben AG, 1984, pages 606 to 607). The use of such conductive lacquers is, however, disadvantageous, due to the elevated organic solvent content thereof.

The object of the present invention is to provide a coating composition for polyolefin substrates, in particular polypropylene blends, in order to overcome the stated

technical disadvantages, which composition is aqueous and, in addition to providing excellent adhesion, allows electrostatic application of subsequent layers. A further object is to reduce the use of chlorinated polyolefins.

This object is achieved by a coating composition based on crosslinking, water-borne two-component resin systems which contain chlorinated and/or non-chlorinated polyolefins and small proportions of organic solvent.

The coating composition according to the invention is characterised in that it contains

10 to 40 wt.%	of one or more polyols having a number average molecular weight of 300 to 2000000, an OH value of 10 to 400 mg of KOH/g and a content of ionic groups and/or groups convertible into ionic groups of up to 400 milliequivalents/100 g of solid resin,
0.5 to 10 wt.%	of one or more chlorinated and/or non-chlorinated polyolefins,
1 to 35 wt.%	of electrically conductive pigments and/or fillers,
5 to 30 wt.%	of one or more organic solvents
25 to 75 wt.%	of water and
1 to 30 wt.%	of polyisocyanates having on average at least two free isocyanate groups per molecule, wherein the sum of the stated constituents is 100 wt.% and the quantity ratio between the polyisocyanate component and the polyol component is selected such that the number of reactive NCO groups to the number of OH groups is in the ratio 5:1 to 0.5:1.

Conventional lacquer additives, further pigments and/or fillers, optionally together with further binders, may also be present. In relation to the resins, the above-stated weight percentages relate to resin solids. Water is the principal solvent.

The coating composition should take the form of a two-component coating composition. One component contains the polyols and the other component the polyisocyanates. The polyol component is in water-borne form and the polyisocyanate component is dispersible in water together with the polyol component. The polyolefins, solvents, optional further binders, pigments, fillers and other lacquer additives may be present in either one or in both of the two components. Care must be taken to ensure the storage stability of the individual components.

The viscosity of the ready-to-apply coating composition may be adjusted to within the desired range by dilution with water.

The quantity ratios of the conductive pigments and/or fillers should be selected such that an adequate subsequent coat may be applied electrostatically. The proportion of these pigments is within a range from 1 to 35 wt.%. The conductive pigments are preferably usable in a quantity of 2 to 30 wt.%

The coating composition according to the invention may crosslink at temperatures as low as room temperature. Crosslinking may be accelerated by adding catalysts or raising the drying temperature. Preferred temperatures are from 40 to 120°C.

The polyol components usable according to the invention are known binders, for example binders based on free-radically polymerisable monomers containing OH groups, polyesters containing OH groups and/or polyurethanes containing OH groups. The number average molecular weight is 300 to 2×10^6, the hydroxyl value 10 to 400. Ionic, nonionic groups or groups convertible into ionic groups may also be present in addition to the OH groups, ester groups, urethane groups. Such groups may be substituents which are cationic or convertible into cationic groups, for example amino groups. Particularly suitable, however, are those substituents which are anionic or convertible into anionic groups, for example carboxyl groups, phosphoric acid groups together with sulphonic acid groups. The content of ionic groups is 400 milliequivalents/100 g of solid resin. The polyol component is in the form of an aqueous dispersion.

Examples of polymers based on free-radically polymerisable monomers are described in EP-A-0 358 979. These may be, for example, styrenes, (meth)acrylic acid alkyl esters, hydroxyalkyl esters of (meth)acrylic acid, monomers containing epoxy or amide groups, such as for example glycidyl (meth)acrylate or N-methoxymethyl (meth)acrylamide. The ionic groups may be introduced by means of olefinically unsaturated monomers having functional groups convertible into ionic groups, for example olefinically unsaturated mono- or dicarboxylic acids, such as for example acrylic acid, maleic acid, itaconic acid and optionally semi-esters thereof or by means of compounds such as 2-acrylamido-2-methylpropane-sulphonic acid. The polymers are produced using known processes, for example by solution polymerisation.

Water-dispersible polyurethane resins are described, for example, in DE-A 41 24 453 and DE-A-40 00 889. The polyurethane resins are produced, for example, by reacting di- or polyhydric saturated linear or branched aliphatic or cycloaliphatic polyalcohols with linear or branched aliphatic, cycloaliphatic or aromatic polyisocyanates and optionally linear or branched aliphatic or cycloaliphatic monoalcohols.

Ionic groups are introduced, for example, by reacting proportions of low molecular weight dialcohols which contain a group which is anionic or capable of forming an anion, preferably a carboxyl group.

The polyurethane polyols preferably have an OH value of 20 to 250. The acid value is 50 to 150, preferably 10 to 60. The number average molecular weight is preferably 2000 to 50000.

Polyester polyols usable according to the invention are, for example, the polyesters described in DE-A-32 13 160, DE-A-28 24 418 and US-A-3 053 783. These may be linear or branched oil-free polyesters based on di- or polyhydric linear or branched aliphatic or cycloaliphatic saturated polyalcohols, together with linear or branched aliphatic, cycloaliphatic or aromatic di- or polybasic carboxylic acids, which may optionally be polycondensed with linear or branched aliphatic monoalcohols.

Usable alcohols preferably contain 2 to 21 C atoms, for example hexanediol, neopentyl glycol, 2,2,4-trimethyl-1,3-pentanediol. The di- or polybasic carboxylic acids preferably contain 5 to 10 carbon atoms, for example isophthalic acid, terephthalic acid, 1,3-cyclohexane-dicarboxylic acid or butylisophthalic acid. Anionic groups

may additionally be incorporated by reaction with low molecular weight dialcohols which additionally contain acid groups capable of forming an anion.

The molecular weight of the polyesters may also be increased by reaction with diisocyanates. Further modifications may optionally be introduced by means of reactive groups, for example OH groups.
The polyester polyols usable according to the invention may advantageously have a molecular weight of 500 to 50000, preferably of 2000 to 50000, particularly preferably of 1000 to 15000 and very particularly preferably of 3000 to 15000.

The OH value is 20 to 200, the acid value 10 to 150.
The polyester polyols are produced using known processes, for example azeotropically or in a melt by a stepwise reaction. Once the desired final values have been achieved, the polyester may optionally be diluted with solvents to achieve a good application viscosity.
The properties of the polyesters may be influenced by means of the dicarboxylic acids or polyalcohols which may be used, for example flexibility may be increased with longer chain aliphatic alcohols or elasticity reduced by introducing aromatic dicarboxylic acids.

Once a proportion of the ionic groups present have been neutralised, the polyols usable according to the invention may be converted into the aqueous phase without further emulsifiers. As a result of the production process, they may still contain small residues of organic solvent. It is, however, also possible to add emulsifiers, wherein the added quantity should be as small as possible.

The polyisocyanates usable according to the invention are conventional, optionally hydrophilised and/or partially blocked lacquer polyisocyanates. They have on average at least two free isocyanate groups per molecule. Such polyisocyanates are described, for example, in EP-A-0 358 979. These are organic polyisocyanates, for example diisocyanates having aliphatically, cycloaliphatically and/or aromatically attached free isocyanate groups. Under certain circumstances, various polyisocyanates may be mixed together. A content of inert solvents may furthermore be added to adjust viscosity. Examples of usable polyisocyanates are known, conventional lacquer polyisocyanates, such as for example hexamethylene diisocyanate, isophorone diisocyanate, tetramethylxylylene diisocyanate.
These may be converted by known processes into oligomers having, for example, biuret, urethane, uretidione or isocyanurate groups.

The composition according to the invention may contain chlorinated and/or non-chlorinated polyolefins.

Chlorinated polyolefins which may be used are conventional commercial materials either individually or as a mixture. These materials may in particular be chlorinated polyethylene, chlorinated polypropylene or chlorinated copolymers thereof having a degree of chlorination of preferably 10 to 45%. The number average molecular weight of the chlorinated polyolefins is preferably 700 to 70000. The chlorinated polyolefins may be used in modified form, for example by incorporation of polar groups, such as for example maleic anhydride. They may be used as resin powder dissolved in an organic solvent or as an aqueous suspension or emulsion.

Alternatively, the content of chlorinated polyolefins may be reduced by using non-chlorinated polyolefins, for example according to DE 43 08 349 and JP 03 122 125 or polyolefin/acrylate copolymers according to DE 44 32 985 having an average molecular weight of 1000 to 50000.

These polymers may optionally also be modified, for example by incorporating polar groups, such as for example maleic anhydride and acrylic acid.

The non-chlorinated polyolefins may be used alone or as a mixture with the chlorinated polyolefins.

The chlorinated and non-chlorinated polyolefins may be used as an aqueous dispersion. As a result of the production process, these may still contain small proportions of organic solvents, together with proportions of ionic or nonionic emulsifiers. The polyolefin fraction may, for example, be added to the coating composition in the form of a dispersion in a similar manner to WO 93/01 244 or WO 90/12 056.

Suitable organic solvents are, for example, conventional lacquer solvents such as ketones, hydrocarbons, alcohols, glycol ethers, such as for example xylene, toluene, mesitylene, benzyl alcohol. The quantity of organic solvents should be kept as small as possible.

The coating compositions according to the invention contain electrically conductive pigments and/or fillers. These pigments or fillers may be inorganic or organic. Commercially available opaque and transparent electrically conductive pigments and/or fillers, as are known, for example, for imparting anti-static properties to polymeric coating materials for appliances, surfaces and components,

may be used. These may be conductively coated TiO_2, barium sulphate, doped tin dioxide, doped zinc oxide (doped, for example, with aluminium, gallium, antimony and bismuth), conductively coated potassium titanate as well as conductive grades of carbon black.

Once the coating composition according to the invention has been applied to the substrate, these substances may produce black to white colours, for example if grades of carbon black or titanium dioxide are used.

Further colours may optionally be achieved by incorporating coloured pigments. Light colours are preferred.

The pigments are preferably ground directly into the polyol component. It is optionally possible, in particular in the case of poorly dispersible pigments, such as for example grades of carbon black, to use a pigment paste using additional binders (grinding resins), for example those based on polyurethane, polyacrylate, polyether and polyester resins. The pigments are finely dispersed therein. The apparatus and methods necessary for this purpose are familiar to the person skilled in the art.

Conductive pigments may be present in the composition according to the invention in a quantity of 1 to 35 wt.%. Preferably, 1 to 5 wt.% of dark to black pigments and 5 to 25 wt.% of grey to light pigments are used.

The coating compositions may optionally contain further pigments and additives. Usable additives are conventional lacquer additives, such as for example wetting agents, dispersion auxiliaries, anti-foaming agents, flow promoters, catalysts, rheological additives together with anti-cratering agents.

The coating compositions according to the invention may optionally additionally contain proportions of further binders which preferably react with the crosslinking components. These may be, for example, aqueous dispersions of polyurethane, polyester, corresponding copolymers or aqueous dispersions prepared from mixtures of such resins, which are preferably mixed into the polyol component.

The coating compositions according to the invention are produced by converting the film-forming resins into the aqueous phase. The materials may be entirely or partially neutralised in order to obtain a stable aqueous emulsion. The polyolefin preparation is preferably present in the binder component, optionally together with the further non-reactive, water-dilutable binders. Additives and/or pigments or fillers may additionally be present in this component.

The second component contains the polyisocyanates. Under certain circumstances, further additives (for example anti-foaming agents) may be present in this constituent. A proportion of the polyolefin preparation may also be incorporated.

The polyisocyanate component is dispersed in the aqueous dispersion of the binder component. The coating composition according to the invention may be adjusted to a suitable application viscosity with water.

Suitable substrates are preferably plastic substrates, in particular modified or unmodified polyolefins. Examples of these are in particular polyethylene or polypropylene substrates together with substrates made from copolymers or mixtures thereof, for example PP/EPDM blends.

The coating composition according to the invention is applied onto the substrate which has preferably not been pretreated and has optionally been cleaned. The coating is then chemically crosslinked, a process which may optionally be supported by an elevated temperature. The crosslinking temperature of the coating composition may be selected depending upon the temperature sensitivity of the substrate as the coating compositions according to the invention are capable of crosslinking over a wide temperature range. A temperature range of 40 to 120°C is preferred.

After crosslinking, homogeneously coated plastic substrates having a faultless surface are obtained, wherein the resultant coatings are distinguished by excellent adhesion to the substrate despite the reduction in CPO content or the use of non-chlorinated polyolefins and by good low temperature impact resistance.

The coating compositions according to the invention are in particular used as electrically conductive keying primers. Further coatings, for example, base lacquer, clear lacquer coatings or single-tone topcoat lacquer coatings may then be applied thereon using electrostatic application methods. These methods permit a distinct reduction in overspray in comparison with conventional application methods.

The resultant multi-layer structures exhibit very good adhesion to the substrate, good low temperature elasticity and no changes in surface appearance on exposure to moisture.

Patent Claims

1. An aqueous two-component coating composition based on one or more polyols and one or more polyisocyanates, in particular for coating plastic substrates, wherein the polyol or polyols is/are present in a first component and the polyisocyanate or polyisocyanates is/are present in a second component and the components are combined before use, characterised in that, once the components have been combined, the coating composition contains the following constituents:

10 to 40 wt.%	of one or more polyols having a number average molecular weight of 300 to 2000000, an OH value of 10 to 400 mg of KOH/g and a content of ionic groups and/or groups convertible into ionic groups of up to 400 milliequivalents/100 g of solid resin,
0.5 to 10 wt.%	of one or more chlorinated and/or non-chlorinated polyolefins,
1 to 35 wt.%	of electrically conductive pigments and/or fillers,
5 to 30 wt.%	of one or more organic solvents
25 to 75 wt.%	of water and
1 to 30 wt.%	of polyisocyanates having on average at least two free isocyanate groups per molecule, wherein the sum of the stated constituents is 100 wt.% and the quantity ratio between the polyisocyanate component and the polyol component is selected such that the number of reactive NCO groups to the

number of OH groups is in the ratio 5:1 to 0.5:1.

2. A coating composition according to claim 1, characterised in that the proportion of conductive pigments and/or fillers is 2 to 30 wt.%.

3. A coating composition according to claim 1 or 2, characterised in that polymers containing OH groups, polyesters containing OH groups and/or polyurethanes containing OH groups are present as the polyol.

4. Use of the coating compositions according to claims 1 to 3 for coating plastic substrates.

5. Use of the coating compositions according to claims 1 to 3 for coating polyolefins.

6. Use of the coating compositions according to claims 1 to 3 for the production of the first layer of a multi-layer lacquer coating on a plastic substrate.

Abstract

The present invention relates to an aqueous two-component coating composition based on one or more polyols and one or more polyisocyanates, in particular for coating plastic substrates, wherein the polyol or polyols is/are present in a first component and the polyisocyanate or polyisocyanates is/are present in a second component and the components are combined before application. Once the components have been combined, the coating composition contains the following constituents:

10 to 40 wt.%	of one or more polyols having a number average molecular weight of 300 to 2000000, an OH value of 10 to 400 mg of KOH/g and a content of ionic groups and/or groups convertible into ionic groups of up to 400 milliequivalents/100 g of solid resin,
0.5 to 10 wt.%	of one or more chlorinated and/or non-chlorinated polyolefins,
1 to 35 wt.%	of electrically conductive pigments and/or fillers,
5 to 30 wt.%	of one or more organic solvents
25 to 75 wt.%	of water and
1 to 30 wt.%	of polyisocyanates having on average at least two free isocyanate groups per molecule, wherein the sum of the stated constituents is 100 wt.% and the quantity ratio between the polyisocyanate component and the polyol component is selected such that the number of reactive NCO groups to the number of OH groups is in the ratio 5:1 to 0.5:1.